

PATENT SPECIFICATION

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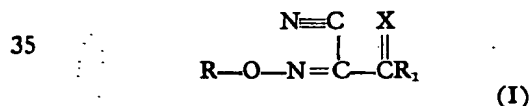
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(54) IMPROVEMENTS IN PESTICIDES

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organized and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns improvements in pesticides, and relates to the use of a class of compound which are of interest in controlling diseases of plants. Fungi and other disease incitants cause extensive losses in crops annually. While there are commercially available materials effective in preventing many plant diseases, still further improvement in this art is needed if full food and fiber production is to be realized. The compounds used in this invention are particularly effective for the control of fungus plant diseases like potato late blight and downy mildews. In addition, the compounds exhibit systemic and curative properties. Relatively small amounts of material can be used to eradicate or cure existing plant disease caused by fungi. This is in contrast to most conventional protective materials which must be applied in advance of attack.

One aspect of our invention provides a composition for combating fungus disease in plants comprising an inert diluent and a compound of the formula



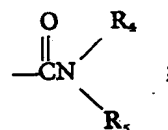
wherein

R is hydrogen; alkyl of 1 to 13 carbon atoms; alkyl of 1 to 13 carbon atoms substituted

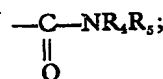
with alkoxycarbonyl of 2 to 4 carbon atoms, acyl of 2 to 4 carbon atoms, acyloxy or 2 to 4 carbon atoms or cyano; acyl of 1 to 4 carbon atoms; alkoxycarbonyl of 2 to 4 carbon atoms; aralkyl of 7 to 10 carbon atoms; or a non-phytotoxic metal e.g. selected from sodium, potassium, calcium, manganese, copper, zinc and iron;

R₁ is alkoxy of 1 to 4 carbon atoms or —NR₂R₃;

R₂ is hydrogen, alkyl of 1 to 4 carbon atoms; alkoxycarbonyl of 2 to 4 carbon atoms or



R₃ is hydrogen or alkyl of 1 to 4 carbon atoms, with the proviso that R₃ is H when R₂ is alkoxycarbonyl or



R₄ and R₅ may be the same or different and are hydrogen or alkyl of 1 to 4 carbon atoms; and

X is oxygen or sulfur; with the proviso that when R² is hydrogen, alkyl or alkoxycarbonyl said composition is not a simple solution of said compound in water or an organic solvent.

Application of these compounds to the locus to be protected from disease effectively combats (i.e. mitigates or prevents) the debility. These compounds are also systemic and curative in plants. Because they are curative, the compounds can be applied before or after the plants to be protected are infected by fungi. This curative activity makes the compounds

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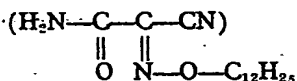


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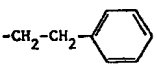
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mp 84—6°, can be prepared by dissolving the sodium salt of 2 - cyano - 2 - hydroxyiminoacetamide in dimethyl formamide. While stirring, 1-iodododecane is added and the solution is heated on the steam bath for six hours. After cooling to room temperature, the solution is poured into water and the precipitate is collected on a filter, washed with water and dried.

The corresponding *n*-octyl derivative, 2-cyano - 2 - *n* - octyloxyiminoacetamide, mp 84—6°, is made from the above sodium salt and 1-bromooctane in the same way. Similarly, the corresponding *n*-decyloxy derivative, 2-cyano - 2 - *n* - decyloxyiminoacetamide, mp 86—7°, made from the above sodium salt and 1-iodo-decane. The tridecyl derivative also melts at 86—7°.

Substituted alkyl derivatives or alkenyl derivatives are made in the same way. The following table lists a number of such materials by way of example:

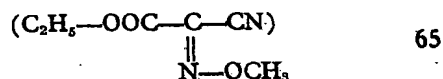
	$\text{H}_2\text{N}-\text{C}-\text{C}-\text{CN}$ $\parallel \quad \parallel$ $\text{O} \quad \text{N}-\text{O}-\text{R}$	
25	$\text{R} =$ 	mp 88 — 9°
	$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CN}$	77 — 80°
	$-\text{CH}_2-\text{COOC}_2\text{H}_5$	143.5—44°
	$\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ -\text{C} \quad \text{C}-\text{CH}_3 \end{array}$	120 — 1°
30	$-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{CH}_3$	90 — 1°
	$-\text{C}^{\text{H}}(\text{CH}_3)-\text{C}_6\text{H}_5$	146 — 7°
	$-\text{CH}_2-\text{CH}=\text{CH}_2$	78 — 9°

N - carbamoyl - 2 - cyano - 2 - methoxyiminoacetamide, mp 161—3°, is similarly prepared from the sodium salt of 2-cyano-2-hydroxy - imino - N - carbamoylacetamide and methyl iodide in DMF.

Additional novel compounds of this invention that are prepared by conventional alkyla-

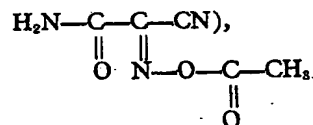
tion, aralkylation, acylation, alkoxycarbonylation and carbamoylation reactions are:

N - carbamoyl - 2 - cyano - 2 - <i>n</i> - octyloxyiminoacetamide, m.p. 75—7°	40
N - carbamoyl - 2 - cyano - 2 - <i>n</i> - dodecyl-oxyiminoacetamide, m.p. 81—4°	45
N - carbamoyl - 2 - cyano - 2 - (3 - phenyl-propyl)oxyiminacetamide, m.p. 108—9°	
N - carbamoyl - 2 - cyano - 2 - acetoxyminoacetamide, m.p. 182—3°	
N - carbamoyl - 2 - cyano - 2 - methoxy-carbonyloxyiminoacetamide, m.p. 183—4°	50
N - carbamoyl - 2 - cyano - 2 - <i>p</i> - chlorophenylcarbamoyloxyiminoacetamide, m.p. 197—200° decomp.	55
N - carbamoyl 2 - cyano - 2 - allylcarbamoyloxyiminoacetamide, m.p. 206—10° decomp.	
N - carbamoyl - 2 - cyano - 2 - (dimethylcarbamoyl)oxyiminoacetamide	60
N - dimethylcarbamoyl - 2 - cyano - 2 - methoxyiminoacetamide	
2 - Cyano - 2 - methoxyiminoacetic acid, ethyl ester	

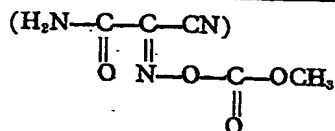


is prepared from the corresponding oxime salt by methylation as described by Muller (Bull. Soc. Chim. [3], 27, 105). The higher homologs of this material can be prepared in the same way from the higher esters of cyanoacetic acid. For example, the *sec*-butyl esters are prepared from *sec*-butyl cyanoacetate via oximation and reaction of the sodium salt of the oxime with the appropriate halide, for example *n*-decyl iodide.

2-Cyano-2-acetoxyminoacetamide



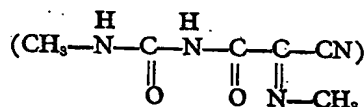
described by Diels and Borgwardt (see above) is conveniently prepared by introducing ketene gas into a solution of 2-cyano-2-hydroxyiminoacetamide in a suitable solvent such as acetonitrile followed by evaporation of the solvent. The higher acyl analogs can be prepared by reaction of the oxime with the appropriate anhydride, for example propionic anhydride, or with the appropriate acyl chloride, for example *n*-butyryl chloride, in the presence of a suitable base such as pyridine or triethylamine. 2 - Cyano - 2 - (methoxycarbonyloxyimino)-acetamide, mp 156—8° dec,



is prepared by adding dropwise methyl chloroformate to an aqueous slurry of the sodium salt of 2 - cyano - 2 - hydroxyiminoacetonitrile with stirring and cooling. The higher alkoxy-

- 5 carbonyl homologs, for example 2 - cyano - 2 - (butoxycarbonyloxyimino)acetamide, are made in the same way from the corresponding higher alkyl chloroformates, e.g., butyl chloroformate.

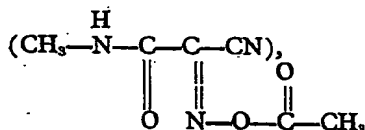
- 10 N - (methyl carbamoyl) - 2 - cyano - 2 - methoxyimino acetamide



is made by nitrosation of the corresponding N - (methyl carbamoyl) - 2 - cyanoacetamide in acetic acid as described in German Patent

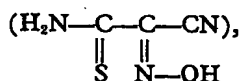
- 15 DRP 227,390 (Frdl 10, 177) followed by methylation of the 2-hydroxyimino intermediate, which is itself a compound of formula I).

- 20 2 - Acetoxymino - 2 - cyano - N - methyl acetamide



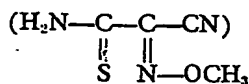
mp 101—3°, is conveniently made by reacting the corresponding free oxime with ketene in acetonitrile. This free oxime (mp 210—1°) is made by nitrosation of N-methyl acetamide.

- 25 2 - Cyano - 2 - hydroxyiminothioacetamide



mp 145° dec, can be prepared from 2-cyanothioacetamide, sodium nitrite and hydrochloric acid as described by G. Shaw and D. N. Butler, J. Chem. Soc. 1959, 4042. The corresponding methyl ester, 2-cyano-2-methoxyiminothioacetamide

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- 35 mp 163—5° can be prepared either by methylation of the oxime with dimethylsulfate in aqueous KOH or by reacting 2-cyano-2-methoxyiminoacetamide in a known manner with

- 40 P₂S₅.

The compounds useful in this invention are active plant disease control agents. They have qualities of systemic and curative activity when applied to soil, to seed or propagation pieces, or to foliage. Combinations with other plant protectants, especially fungicides, provide exceptional disease control. The systemic and curative properties of the disease control agents of this invention make their combination with fungicides usually result in more than an additive effect. For this reason, compositions containing a combination of a fungicide and a compound of this case are preferred. The marked systemic property of the compounds of this case is strikingly evident by the control of the potato late blight disease on the untreated foliage when treatments with the compounds of this invention are applied solely to the root system. Additional evidence comes from the protection of untreated new growth on plants which had previously been sprayed with the compounds of this invention. Still further evidence comes from the curative action against established infections by the causal agent of late blight-disease. The disease can be arrested even when treatments are delayed hours after plants have been artificially inoculated.

Of the fungi causing diseases on agricultural crops, those classed as Phycomycetes are among the most virulent. The disorders caused by this group of fungi include late blight of tomatoes and potatoes, downy mildew of grapes and cucurbits, and *Pythium* root rots. Diseases caused by Phycomycetes are especially susceptible to control by the compounds of this invention. Many other plant diseases of primary importance to the agriculturist are also controlled.

The many diseases (along with their causal agents) against which the compounds and methods of this invention are effective may be represented by, but are not limited to, the following: *Phytophthora infestans*, which causes late blight of potato and tomato; *Phytophthora cinnamomi*, which causes root rot of many perennial plants and heart rot of pineapple; *Alternaria solani*, which attack plants in the Cruciferae, Cucurbitaceae, Umbelliferae, and Solanaceae families; and *Venturia inaequalis*, which causes apple scab.

The compounds of this invention provide protection from damage caused by certain fungi when applied to the proper locus by the methods described hereinafter and at a sufficient rate to exert the desired effect. They are especially suited for the protection of living plants by applying the compounds of this invention to the soil in which they are growing or in which they may subsequently be seeded or planted, to seeds, tubers, bulbs, or other plant reproductive parts prior to planting, as well as to foliage, stems, and/or fruit. Soil

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applications are made from dusts, granules, pellets, solutions, or slurries.

5 Preferred rates for application of the compounds of this invention to soil in which plants are or will be growing range from 1 to 500 parts per million by weight of the soil in which the roots are or will be growing. More preferred use rates are in the range of 5 to 200 parts per million. The most preferred rates are in the range of 10 to 100 parts per million. Preferred rates for application to seeds, tubers, bulbs, or other plant reproductive parts range from 0.5 to 100 grams of active compound of this invention per kilo of planting material treated. More preferred rates are in the range of 1 to 75 grams of active compound per kilo. The most preferred rates are in the range of 2 to 50 grams per kilo. Applications of this type are made from dusts, slurries, or solutions.

20 Preferred rates of application for the compounds of this invention to foliage, stems, and/or fruit of living plants range from 0.1 to 20 kilograms of active ingredient per hectare. More preferred rates are in the range of 0.2 to 10 kilos per hectare. The most preferred rates are in the range of 0.5 to 5 kilograms per hectare. The optimum amount within this range depends upon a number of variables which are well known to those skilled in the art of plant protection. The variables include, but are not limited to, the disease to be controlled, weather conditions expected, the type of crop, stage of development of the crop, and the interval between applications. Applications within the range given may need to be repeated one or many more times at intervals of 1 to 60 days. Applications are made from dusts, slurries, or solutions.

40 The compositions of the invention can contain, in addition to the active ingredient of this invention, conventional insecticides, miticides, bactericides, nematocides, fungicides, or other agricultural chemicals such as fruit set agents, fruit thinning compounds, fertilizer ingredients and the like. The additional agricultural chemicals are employed in mixtures or combinations in amounts ranging from one-tenth to twenty times that of the compound or compounds of this invention. The proper choice of amounts is readily made by one skilled in the art of protecting plants from pest depredations. The following are illustrative of the agricultural chemicals that may be included in compositions of the compounds of this invention or, additionally, that may be added to sprays containing one or more of the active compounds of this invention:

60 bis(dimethylthiocarbamoyl)disulfide; or tetramethylthiuram disulfide (thiram); metal salts of ethylenebisdithiocarbamic acid or propylenebisdithiocarbamic acids, e.g. manganese, zinc, iron and sodium salts (maneb or zineb); *n*-dodecylguanidine acetate (dodine);

N - (trichloromethylthio)phthalimide (folpet);

N - [(trichloromethyl)thio] - 4 - cyclohexene-1,2-dicarboximide (captan);

cis - N - [(1,1,2,2 - tetrachloroethyl)thio] - 4-cyclohexene-1,2-dicarboximide (captafol);

2,4 - dichloro - 6 - (o - chloroaniline) - s-triazine ("Dyrene");

3,3' - ethylenebis(tetrahydro - 4,6 - dimethyl - 2H - 1,3,5 - thiadiazine - 2 - thione), (milneb);

triphenyltin hydroxide (fentin hydroxide);

triphenyltin acetate (fentin acetate);

N' - dichlorofluoromethylthio - N,N - dimethyl - N' - phenylsulfamide (dichlofluamid);

tetrachloroisophthalonitrile (chlorothalonil);

tribasic copper sulfate;

fixed copper;

sulfur;

methyl - 1 - (butylcarbamoyl) - 2 - benzimidazolecarbamate (benomyl);

methyl-2-benzimidazolecarbamate;

1,2 - bis(3 - methoxycarbonyl - 2 - thio-ureido)benzene (methyl thiophanate);

The agricultural chemicals listed above are merely exemplary of the compounds which can be mixed with the active compounds of this invention and are not intended to any way limit the invention.

The use of pesticides in combination with a compound within the scope of this invention sometimes appears to greatly enhance the activity of the active compound of the invention. An unexpected degree of activity is sometimes seen when another pesticide is used along with the methods of this invention.

The useful compounds can be applied in a variety of formulations, including wettable powders, water-soluble powders, suspensions, emulsifiable concentrates, dusts, solutions, granules, pellets, etc. High strength compositions may also be prepared for use by local formulators in further processing.

These formulations include one or more compounds useful in this invention, and can include surface-active agents, solid or liquid diluents and other materials as required to produce the desired formulation.

The surface-active agents act as wetting, dispersing and emulsifying agents which assist dispersion of the active material in a spray, and improve wetting of waxy foliage and the like by the spray. Thus they aid in convenience, accuracy and effectiveness in use. The surfactants can include such anionic, non-ionic and cationic agents as have been used heretofore in pesticidal compositions of similar type. A detailed list of such agents may be found in "Detergents and Emulsifiers Annual", (John W. McCutcheon, Inc.). Addition of surfactants also prevents precipitation of large crystals of the active compounds on plant surfaces and improve penetration of the active compounds,

thus increasing activity. Anionic and non-ionic surfactants are preferred. Such preferred surfactants include alkali and alkaline earth salts of alkylarylsulfonic acids, such as dodecylbenzenesulfonates and alkylphenylenesulfonates, dialkyl sodium sulfosuccinate esters, sodium lauryl sulfate, sodium N-methyl-N-oleoyltaurate, sodium dodecylphenyl ether disulfonate and the oleic acid ester of sodium isethionate. Other preferred surfactants include alkyl and alkylphenyl polyethylene glycol ethers, and their phosphate derivatives, polyoxyethylene derivatives of sorbitan fatty esters and long-chain alcohols and mercaptans, as well as polyoxyethylene esters of fatty acids. Film forming water-soluble polymers may be used in place of surfactants to improve activity. Humectants and oils chosen for low phytotoxicity also contribute to enhanced activity of the compositions of this invention. White oils having a viscosity of about 150 S.S.U. or higher are preferred.

Further information on formulation of the active compounds described above into the fungicidal compositions of this invention can be found in J. B. Buchanan, U.S. 3,576,834 (4/27/71), R. R. Schaffen, U.S. 3,560,616 (2/2/71) and E. Somers, "Formulation", Chapter 6 in Torgeson, "Fungicides", Vol. I, Academic Press, New York, 1967.

The following examples further illustrate the invention. All parts and percentages are by weight.

EXAMPLE 1.

A wettable powder formulation can be made and applied as follows:

	Percent
2-cyano-2-hydroxyimino-acetamide	50
sodium alkylphenylenesulfonate	2
low-viscosity methylcellulose	2
diatomaceous earth	46

The ingredients are blended, coarsely hammer-milled and then air-milled to produce particles of active essentially all below 20 microns in diameter. The product is rebled before packaging.

All compounds of the invention may be formulated similarly.

This formulation is dispersed in water in an amount sufficient to provide a concentration of 400 ppm of the active compound of this invention. A portion of this is diluted to a concentration of 80 ppm. The dispersions are sprayed to the point of run-off on potted tomato plants and allowed to dry. Both treated and untreated plants are inoculated with a spore suspension of *Phytophthora infestans* and incubated for a day in a saturated humidity chamber. After five days of additional incuba-

tion in the greenhouse, all of the untreated tomatoes are dead because of late blight disease. The plants treated with the 80 ppm concentration have only an occasional confined lesion, whereas those treated with the 400 ppm concentration are completely healthy with no sign of disease. The other compounds of this invention can be substituted for 2-cyano - 2 - hydroxyiminoacetamide with like results. For example, N - carbamoyl - 2-cyano - 2 - methoxyiminoacetamide and 2-acetoxyimino - 2 - cyano - N - methyl acetamide are particularly effective.

EXAMPLE 2.

The formulation of Example 1 can be mixed in a spray tank with the fungicide, benomyl. This formulation is diluted to a concentration of 500 ppm of the active ingredient. The benomyl in the mixture is at a concentration of 100 ppm. Sprays are applied to the point of run-off each week during the growing season to a cucumber field subject to infection by the downy mildew fungus, *Pseudoperonospora cubensis*, the powdery mildew fungus, *Erysiphe chichoracearum*, and the gummy stem blight fungus, *Mycosphaerella citrullina*. The plants which are sprayed with this mixture are healthy and bear a normal crop.

EXAMPLE 3.

Potted greenhouse grown tomato plants are inoculated by spraying them with a spore suspension of *P. infestans*. They are incubated in a saturated humidity chamber for eight hours. The infected tomato plants are removed from the incubation chamber long enough to spray them with various disease control agents and combinations of these agents. The formulation of Example 1 is dispersed at a concentration of 400 ppm of the active ingredient. Similar dispersions are made of the commercial fungicides, maneb, captafol, metiram, and chlorothalonil. Additional treatments are made by mixing each of these dispersions of commercial fungicides with an equal quantity of the formulation of this example. This results in 200 ppm of each of the two component active ingredients. Six infected plants are sprayed with enough dispersion to have run-off of dry plants. After treatment, the plants are returned to the humidity chamber for a total of 24 hours. After an additional five days incubation in the greenhouse, the untreated plants are dead because of the late blight disease. Those plants treated with the commercial fungicides are completely defoliated. The plants treated with the formulation of this invention have only a few restricted lesions. Most of the foliage is healthy. This is because of the unique curative action of the compounds of this invention. The best control is afforded by the mixtures of commercial fungicides and the 2 - cyano - 2 - hydroxyiminoacetamide.

EXAMPLE 4.

Healthy uninoculated tomato plants are spray treated with the suspensions and mixtures prepared for the curative test described in Example 3. The treated plants are grown for five days in the greenhouse before they are inoculated with a spore suspension of *P. infestans*. The plants had grown sufficiently from the time they were treated to expose untreated foliage. After incubation, the untreated plants are dead because of late blight infections. The commercial fungicides provide good control on most of the foliage, but the newly expanded foliage is unprotected and is heavily blighted. The plants sprayed with the formulation of this invention have only a few blight lesions. The most striking feature is the reduction in infections on the newly expanded foliage. This is because of the systemic property of protecting untreated plant parts afforded by the compounds of this invention. Those plants which are treated with mixtures of 2 - cyano - 2 - hydroxyiminoacetamide and commercial fungicides at one-half rate of each are the healthiest of all.

EXAMPLE 5.

A wettable powder formulation can be prepared as follows:

	Percent
30 N-carbamoyl-2-cyano-2-methoxyiminoacetamide	80
sodium alkyl naphthalenesulfonate	2
sodium ligninsulfonate	2
synthetic amorphous silica	3
35 Kaolinite	13

The ingredients are thoroughly blended, passed through a hammer-mill to produce an average particle size under 40 microns, reblended and sifted through a U.S.S. No. 50 sieve (0.3 mm openings) before packaging.

This formulation can be applied as follows: A potato field is selected in which there is a uniform but light infection of the late blight disease. The older foliage of each plant supports one or two sporulating *Phytophthora infestans* lesions. The plant damage at this point is slight, but the potential for disease spread is high. Plots are designated as five rows wide and 20 meters long. Treatments are assigned to various plots randomly through the field leaving much of the field untreated as buffers between treated plots. A series of treatments is selected for application immediately following weather conditions conducive to disease spread. Among those treatments is the formulation of this Example dispersed in water at a concentration of 1,000 ppm. of active ingredient. Other treatments are a representation of commercially available fungicides such as

maneb, captafol, and chlorothalonil, applied at their recommended use rate. In addition to these single compound applications, combinations of the formulation of this Example with each of the commercial fungicides are made at rates of 1/2 of that used alone. Spray applications are made immediately after an overnight rain which had the potential of spreading the disease. After a week, the untreated foliage in this field is completely killed by the late blight disease. Those plots receiving treatments of commercial fungicides are severely diseased and are more than 80% defoliated. Those plots receiving the formulation of this Example are protected from the late blight disease and are only slightly defoliated. Those plots receiving the combination of the formulation of this invention plus a commercial fungicide are healthy and green and free of disease. Other commercial fungicides such as metiram, "Daconil 2787" and zineb, can also be used with like results. The other compounds of this invention may be substituted for 2-cyano-2-hydroxyiminoacetamide with like results.

EXAMPLE 6.

An aqueous suspension can be prepared and applied as follows:

	Percent	
2-cyano-2-dodecyloxyiminoacetamide	25	90
hydrated attapulgit	3	
crude calcium ligninsulfonate	10	
disodium hydrogen phosphate	0.5	
water	61.5	

The ingredients are ground together in a ball or roller mill until the solid particles have been reduced to diameters under 10 microns.

This suspension is dispersed in water in an amount sufficient to provide a concentration of 400 ppm of the active compound of this invention. A portion of this is diluted to a concentration of 80 ppm. The dispersions are sprayed to the point of run-off on potted apple plants and allowed to dry. Both treated and untreated plants are inoculated with a spore suspension of *Venturia inaequalis* and incubated for a day in a saturated humidity chamber. After ten days of additional incubation in the greenhouse, all of the untreated apples have young susceptible leaves completely recovered with sporulating apple scab lesions. The plants treated with the 80 ppm concentration have only an occasional confined lesion, whereas those treated with the 400 ppm concentration are completely healthy with no sign of disease.

EXAMPLE 7.

An oil suspension can be prepared as follows:

	Percent
2-cyano-2-hydroxyiminoacetamide	25
polyoxyethylene sorbitol hexaoleate	5
highly aliphatic hydrocarbon oil	70

- 5 The ingredients are ground together in a sand mill until the solid particles have been reduced to under about 5 microns. The resulting rather thick suspension may be applied directly, extended with oils, or emulsified in water.

- 10 This formulation can be applied in the same manner as the wettable powder formulation of Example 5 with similar results.

EXAMPLE 8.

- 15 An emulsifiable concentrate can be prepared and applied as follows:

	Percent
2-cyano-2-dodecyloxyiminoacetamide	30
isophorone	65
20 blend of oil-soluble sulfonates and polyoxyethylene ethers	5

- 25 The ingredients are combined and stirred with gentle warming to speed solution. A fine screen filter is included in the packaging line to insure the absence of any undissolved matter in the final product.

- 30 The above formulation is dispersed in water to give an active ingredient concentration of 800 ppm. Eight uniform grapevines of the same variety are sprayed to run-off at weekly intervals during the growing season with the above formulation. Untreated vines growing near are severely infected with the downy mildew fungus, *Plasmopara viticola*. The eight treated vines are healthy with a normal crop of disease free fruit.

EXAMPLE 9.

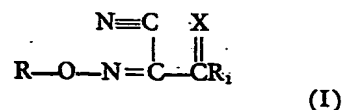
High-strength powder.

	Percent
40 2-cyano-2-hydroxyimino acetamide	90.0
fine silica	9.5
dioctyl sulfosuccinic acid, disodium salt	0.5

- 45 This powder is prepared by blending and then grinding in a hammer-mill. The formulation, when dispersed in water, causes the active ingredient to go into solution. The spray can be used in a manner similar to Example 5.

WHAT WE CLAIM IS:—

- 50 1. A composition for combating fungus disease in plants comprising an inert diluent and a compound of the general formula



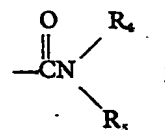
wherein

R is hydrogen; alkyl of 1 to 13 carbon atoms; 55

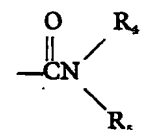
alkyl of 1 to 13 carbon atoms substituted with alkoxyacetyl of 2 to 4 carbon atoms, acyl of 2 to 4 carbon atoms, acyloxy of 2 to 4 carbon atoms or cyano; acyl of 1 to 4 carbon atoms; alkoxyacetyl of 2 to 4 carbon atoms; aralkyl of 7 to 10 carbon atoms; 60

or a non-phytotoxic metal;
R₁ is alkoxy of 1 to 4 carbon atoms or —NR₂R₃;

R₂ is hydrogen, alkyl of 1 to 4 carbon atoms, alkoxyacetyl of 2 to 4 carbon atoms or 65



R₄ is hydrogen or alkyl of 1 to 4 carbon atoms with the proviso that R₄ is H when R₅ is alkoxyacetyl or 70

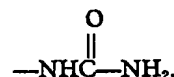


R₄ is hydrogen or alkyl of 1 to 4 carbon atoms; R₅ is hydrogen or alkyl of 1 to 4 carbon atoms; and

X is oxygen or sulfur; with the proviso that when R² is hydrogen, alkyl or alkoxyacetyl, said composition is not a simple solution of said compound in water or an organic solvent. 75

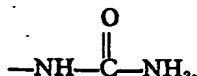
2. The composition of claim 1 wherein R is as defined in claim 1 with the proviso that when R is a non-phytotoxic metal it is selected from sodium, potassium, calcium, manganese, copper, zinc and iron. 80

3. The composition of claim 2 wherein X is oxygen; R is hydrogen, alkyl of 1 to 13 carbon atoms, acyl of 1 to 4 carbon atoms, alkoxyacetyl of 2 to 4 carbon atoms, or a metal selected from sodium, potassium, calcium, manganese, zinc, copper and iron; and R₁ is —NH₂, —NHCH₃ or 85



4. The composition of claim 3 wherein R is hydrogen, alkyl of 1 to 13 carbon atoms, or acetyl. 90

5. The composition of claim 4 wherein R_1 is $-\text{NH}_2$, $-\text{NHCH}_3$ or



6. The composition of claim 1 wherein said compound is 2 - cyano - 2 - hydroxyiminoacetamide or a salt thereof with a non-phytotoxic metal.
7. The composition of claim 5 wherein said compound is 2-cyano-2-methoxyiminoacetamide.
8. The composition of claim 5 wherein said compound is N - carbamoyl - 2 - cyano - 2-methoxyiminoacetamide.
9. The composition of claim 5 wherein said compound is 2 - acetoxyimino - 2 - cyano - N-methyl acetamide.
10. The composition of claim 1 wherein said compound is N - (methyl - carbamoyl) - 2-cyano-2-methoxyimino acetamide.
11. The composition of claim 1 wherein said compound is a compound of general formula I as hereinbefore specifically disclosed other than those defined in claims 6—10.
12. The composition of any of the preceding claims including one or more insecticides, miticides, bactericides, nematocides, fruit set agents, fruit thinning compounds or fertilizers.
13. The composition of any of the preceding claims including one or more fungicides

other than those of the general formula I herein. 30

14. The composition of claim 13 wherein said one or more fungicides is selected from those specifically disclosed hereinbefore.

15. The composition of any of the preceding claims containing an adjuvant selected from surfactants, water soluble film-forming polymers, humectants and non-phytotoxic oils. 35

16. The composition of claim 1 substantially as hereinbefore described and as illustrated with reference to any of the Examples. 40

17. A method of combating fungus disease in plants which comprises applying to the locus to be protected an effective amount of a compound as defined in claim 1. 45

18. The method of claim 17 wherein there is applied a compound as defined in claim 2.

19. The method of claim 17 wherein there is applied a compound as defined in any of claim 3 to 5 or 11. 50

20. The method of claim 17 wherein there is applied a compound as defined in any of claims 6—10 or the composition of claim 13 or 14 as appendant to any of claims 6 to 10.

21. The method of claim 17, substantially as described herein and as illustrated with reference to any of the Examples. 55

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